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**METHOD FOR PREPARATION OF FINE POWDERED
CELLULOSE ETHERS**

Field of the Invention

5 The present invention relates to a method for the preparation of fine powdered cellulose ethers. In particular, the present invention relates to a method of preparation of cellulose ethers in a cost-effective manner having high running efficiency of process, which specifically regulates a reaction condition of each step to induce a particle refinement and thus significantly reduces a running load on a
10 grinding process, in the reaction of treating finely pulverized celluloses with a caustic soda and reacting with an etherifying agent.

Background of the Invention

Cellulose ethers, such as alkylcellulose and hydroxyalkylcellulose,
15 hydroxyalkyl alkylcellulose are industrially valuable compounds used as thickeners, binders or adhesives in such diverse applications of medicine, construction industry, paints and so on.

Numerous methods have been disclosed as methods for preparing the cellulose ethers as follows.

20 US Pat. No. 4,076,935 discloses a method of reducing the particle size of cellulose ethers which comprises grinding the manufacture cellulose ethers in a vibration mill in the presence of air and sufficient water to yield a product, wherein at least 50% of the particles in the product are in a particle size of 100 micron or less. However, the method has several problems of requiring the use of complicated and
25 special equipment, i.e., a vibration mill, and increasing a bulk weight of a product

due to the additional injection of water.

In addition, US Pat. No. 4,820,813 teaches a method of producing high viscose cellulose ether particles with a fine particle size by impacting with a high speed air-swept impact mill. The cellulose ether products, after grinding, becomes
5 very fine granules with a size of from about 40 to 400 mesh, but there is also a problem with this method that it requires a specific mill and manufactured good.

Further, US Pat. No. 5,488,104 discloses a process for comminuting cellulose ethers which comprises extruding the synthesized cellulose ethers through a plurality of orifices, each orifice having a cross-sectional area of from about 7.5×10^{-9}
10 m^2 to about $1 \times 10^{-6} m^2$, to form an elongated extrudate, cutting the elongated extrudate to a desired length, and then grinding it with an air-swept impact mill. However, since this method requires more time for the process increased due to the introduction of a process of extruding a product with a microporous filter, it is very difficult to completely wash the filter, and the overall process of repeating the
15 cutting, drying and grinding steps is very complicated and also not favored from the industrial point of view.

Furthermore, US Pat. No. 4,415,124 teaches two different methods for the production of micropowder from cellulose ethers, wherein one method comprises subjecting the cellulose ethers to a consolidation in a cooled ball mill and passing the
20 consolidated material through a jet mill; and the other comprises, compressing the cellulose ethers into a pellet and grinding the pellet with a jet mill or a impact disc mill. However, since these methods should use at least two different mills in the grinding step, it increases the cost for equipments and the time required for the process. They are also industrially inefficient because it is possible to bring the
25 overall process to a halt due to clogging occurred in the previous step. In addition,

these methods have serious drawbacks that it requires considerable expenses for its operation, maintenance and repair.

Therefore, the known methods for the preparation of cellulose ethers described above have several problems that, although they suggest the use of a 5 special equipment in the drying and grinding steps, this would make the investment scale enlarged, and there is a limitation with regard to capacity for applying to mass production since they require a pre-treatment step of compression and extrusion prior to the pulverization. Besides, the disadvantages of the known methods are complication of process and difficulty in maintenance.

10 Meanwhile, the present inventors have filed a patent application relating to a method for the preparation of cellulose ethers, which carries out the washing and filtering steps at the same time and introduces a process performing the grinding and drying steps simultaneously (Korea Patent Laid-Open Publication No: 2003-42796). The above method has the advantage of simultaneously performing the 15 grinding and drying steps, but it is also requires a certain equipment for reducing the particle size, e.g., a mill, which incurs additional expenses for its operation, maintenance and repair.

The present inventors have therefore endeavored to solve theses problems of the known methods and as a result have found a reaction condition for preparing a 20 microparticle form of cellulose ethers through a reactive control study for a synthetic process of cellulose ethers and developed a method for the preparation of fine powdered cellulose ethers which regulates the product's configuration by controlling the amount of an organic reactant in a reaction system.

Summary of the Invention

Accordingly, an object of the present invention is to provide an industrially efficient and economical method for the preparation of fine powdered cellulose ethers.

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Detailed Description of the Invention

In accordance with one aspect of the present invention, there is provided a method for the preparation of fine powdered cellulose ethers comprising the steps of dispersing a caustic soda in pulverized celluloses and adding an etherifying agent thereto, which is characterized in that after 0.01 to 3.0 parts by weight of the etherifying agent based on 1 part by weight of cellulose is fed to a reactor, the reaction mixture is subjected to a primary reaction in the condition of gradually increasing temperature ranging from 40 to 60°C for 10 to 60 min, a secondary reaction in the condition of gradually increasing temperature ranging from 45 to 10 75°C for 60 to 180 min, and a tertiary reaction in the condition of gradually increasing temperature ranging from 80 to 90°C for 60 to 180 min in order.

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In particular, there is provided the method for preparing the fine powdered cellulose ethers which is characterized by comprising the steps of

- (i) subjecting the pulverized celluloses to alkalinization by treating 20 with an alkalinizing agent;
- (ii) preparing a reaction mixture by adding 0.01 to 3.0 parts by weight of an etherifying agent based on 1 part by weight of cellulose to the alkalinized celluloses;
- (iii) subjecting the reaction mixture to the primary reaction in the 25 condition of gradually increasing temperature ranging from 40 to

60°C for 10 to 60 min;

5 (iv) subjecting the primary reaction mixture to the secondary reaction in the condition of gradually increasing temperature ranging from 45 to 75°C for 60 to 180 min; and

(v) subjecting the secondary reaction mixture to the tertiary reaction in the condition of gradually increasing temperature ranging from 80 to 90°C for 60 to 180 min.

Hereinafter, the present invention is described in detail.

10 The present invention relates to the economical method for the preparation of cellulose ethers having high running efficiency of process, which comprises specifically regulating a reaction condition of each step to induce a particle refinement and significantly reduces a running load on a grinding process in the reaction of treating finely pulverized celluloses with a caustic soda and reacting with
15 an etherifying agent.

In the inventive method for the preparation of cellulose ethers, for the reaction of cellulose with an etherifying agent, it must be preceded an alkalinization by treating with the alkalifying agent to mollify a hard crystal structure of cellulose. The alkalifying agent plays a role of stimulating a binding or a reaction of various
20 chemical compounds to the cellulose by expanding the crystal structure of cellulose via a binding to the cellulose as well as functions as a catalyst in the reaction of cellulose and an etherifying agent.

The active alkalinized celluloses are subjected to stirring at room temperature for a predetermined time to finely mollify its crystal structure.

25 After the celluloses alkalinized at room temperature are kept at a constant

state capable of binding to a reactant, the etherifying agent is added thereto, and then, binds to the celluloses. There are some differences in the treatment of caustic soda to obtain a Degree of Substitution (DS) of a desired reactant (generally, alkyleneoxide and alkylhalide). The amount of treated caustic soda in the present
5 invention varies to obtain the Degree of Substitution (DS) of alkoxy percent ranging from 15 to 30% and hydroxyalkoxy percent ranging from 5 to 25%.

Further, the inventive method of the presentation for preparing fine powdered cellulose ethers may comprise adding a diluent gas as a selective step before the step (ii) treating with the etherifying agent. However, it is preferable not
10 to use a diluent gas or use it with a trace amount to produce cellulose ether with improved quality.

The diluent gas to be used in the present invention may be synthesized by using an ether compound such as dimethylether and a low grade alcohol such as isopropanol. However, the etherifying agent and diluent gas must be used with a
15 fixed amount to obtain the desired Degree of Substitution. The configuration of the synthesized cellulose particles may differ according to the amount of an etherifying agent and a diluent gas and a reaction temperature. Some cellulose ethers have a light fibrous shape and the others, a spherical shape, which affects the Degree of Substitution or transparency of a product. Further, for the commercialization of
20 theses cellulose ethers, it is required to induce granulation by treating with cold water, followed by drying, grinding with a jet mill or a ball mill to obtain a desired particle size, and then filtering them through a sieve having a predetermined pore size.

In case of synthesizing the cellulose ethers in a fibrous shape having a low
25 density using a conventional preparation method, the granulation is not proceeded

smoothly, and thus the bulk density of product may be worsened, which leads to increase in the amount of recirculation in the grinding and distribution steps and curtail the productivity. In case of synthesizing them in a spherical shape, the cellulose ethers can be well granulated. However, when an interior of the particle
5 is not completely substituted with the etherifying agent or hydrophobic components are accumulated in its interior, they are arranged toward the surface for the pulverization and finally form a fibrous shape, which results in the disadvantages in the process that while an bulk density of the product may be deteriorated, the amount of recirculation in the grinding step may increase.

10 Accordingly, the present inventors have endeavored to solve theses problems and developed a method for preparing the cellulose ether particles having a hard fibrous shape, which is possible by controlling the total amount of organic compounds and a reaction temperature in a reaction system. Namely, the amount of organic compound means the total amount of organic matters including the
15 injected etherifying agent based on the amount of finely pulverized cellulose ethers, and the reaction temperature, a step of maintaining or cooling the reactor's temperature after all the organic compounds are injected into a reactor and the reactor's temperature is gradually increased for a predetermined time. The configuration of cellulose ether particles can be regulated according to the
20 combination of the amount of organic compounds and a reaction temperature.

The method of the present invention is described in more detail as follows.

The hard crystal structure of cellulose must be mollified to react with the etherifying agent. For this, it is preferable to use alkali metal hydroxide (caustic
25 soda) in a solid or an aqueous solution state. In particular, it is more preferable to

use sodium hydroxide, potassium hydroxide or lithium hydroxide. It is important to spray the caustic soda to the pulverized celluloses to be evenly distributed. After the caustic soda is completely sprayed, less than 2.5 parts by weight of the diluent gas is injected for 1 part by weight of cellulose and well mixed, wherein the diluent
5 gas may be selected from the group of ester compounds such as dimethylether and diethylether. More preferably, the diluent gas is injected less than 2.0 parts by weight for 1 part by weight of cellulose. If it exceeds 2.5 parts by weight, it can be dangerous because it is possible that the reactor's pressure goes beyond the maximum point. After the injection of a diluent gas, alkyleneoxide and alkylhalide
10 are injected as an etherifying agent. It is preferable to use ethyleneoxide, propyleneoxide and butyleneoxide having a carbon atom ranging from 2 to 4 as alkyleneoxide, and methylchloride, ethylchloride, propylchloride and butylchloride having a carbon atom ranging from 1 to 5 as alkylhalide. Further, it is preferable that the etherifying agent is injected in the range of from 0.01 to 3.0 for 1 part by
15 weight of cellulose. If the etherifying agent is injected less than 0.01 part by weight, it is very difficult to control the reaction temperature and a rapid exothermic reaction may be occurred. If the etherifying agent is injected more than 3.0 parts by weight, it is difficult to operate the process due to an excessive increase in reactive pressure and thus a special high pressure reactor is needed. After all the
20 etherifying agent is injected, the primary reaction is carried out in the condition of gradually increasing temperature ranging from 40 to 60°C (preferably, from 40 to 50°C) for 10 to 60 min. If the temperature is below 40°C, the reaction rate becomes slowed down, which leads to the increase in time required for the process. In contrast, if the temperature is higher than 60°C, it is difficult to control the reaction of
25 alkyleneoxide, which generates a lot of by-products due to a local overheating

phenomenon. In case the reaction time is less than 10 min, a rapid exothermic reaction occurs due to extremely rapid temperature increase, which makes difficult to control the reaction temperature. In case the reaction time is more than 60 min, the overall process requires a longer period of time.

5 Further, the secondary reaction is performed in the condition of gradually increasing temperature ranging from 45 to 75°C (preferably, from 55 to 65°C) for 60 to 180 min. If the temperature is below 45°C, the progress of the reaction becomes too slow, and if the temperature is higher than 75°C, the production of by-products increases. If the reaction is performed for less than 60 min, the amount of
10 unreacted alkyleneoxide increases, and if it is performed for more than 180 min, the reactive products may be denatured.

Then, the tertiary reaction is carried out in the condition of gradually increasing temperature ranging from 80 to 100°C (preferably, from 85 to 90°C) for 60 to 180 min and maintaining the resulting temperature for 10 to 60 min. In case of
15 the temperature is below 80°C, it is difficult to completely react the celluloses with alkylhalide, and if it is higher than 100°C, the synthesized products may undergo a change in its color and degradation. In case the reaction is performed for less than 60 min, the alkylhalide reaction is not sufficient, and if it is performed for more than 180 min, the synthesized products may be denatured. After the reaction is
20 completed, the synthetic products are subjected to filtering with 95°C hot water, injected into a mill, where 60 to 80°C hot wind blows is provided, and immediately distributed without a load of grinding treatment, to obtain fine powdered cellulose ethers.

Since the cellulose ether particles are prepared in a fibrous shape according
25 to the inventive method, they do not conglomerate into a flock for drying, which

5 prevents the enlargement of particle size. Further, since the particles are very flexible, they can be easily separated by a simple air-flow into a pipe, which guarantees the maintenance of product's feature for synthesis. Accordingly, the physical properties of the fine powdered cellulose ethers of the present invention are significantly different from those of cellulose ethers prepared by the conventional methods.

10 Further, the bulk density of the cellulose ethers obtained after simple drying is ranging from 0.45 to 0.65 g/mL. From the result, it has been found that the inventive method can prepare the cellulose ethers having a high bulk density without the additional granulation process. In addition, the cellulose ether particles prepared by the inventive method in the state of drying without the grinding step have the particle size distribution with 99 to 100% by weight of less than 100 mesh. At this time, a water content of the cellulose ether particles is regulated to be less than 3.0%.

15 These results have confirmed that the cellulose ether particles prepared by the inventive method are already formed in a microparticle shape. The method for the preparation of cellulose ethers of the present invention is industrially efficient and economical since there is no need of vigorously controlling the running condition of a mill, it is possible to reduce the time required for the process due to no recirculation of oversized products in the distribution process, and thereby, the running load is significantly decreased.

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25 The following Examples and Test Examples are given for the purpose of illustration purposes only and shall not be construed as limiting the scope of the invention.

Example 1

6 kg of finely pulverized celluloses were fed into a high-pressure reactor whose capacity is 100L of volume. To react the celluloses with an etherifying agent, 5 a caustic soda in 50% by weight of an aqueous solution was evenly dispersed in the reactor by spraying to mollify the hard crystal structure of cellulose. After 8 kg of the caustic soda was completely sprayed, 2 kg of dimethylether as a diluent gas was injected into the reactor and mixed well. At this time, 2.5 kg of ethyleneoxide and 8 kg of methylhalide were added thereto. After the mixture was reacted for 60 10 min until the temperature reached 40°C, it was subjected to a secondary reaction in the condition of gradually increasing temperature ranging from 40 to 75°C for 100 min and a tertiary reaction at temperature of 80°C for 3 hrs, and then, the reactor's temperature was maintained for 30 min.

After the reaction was completed, 100L of hot water was fed to the reactor 15 and stirred for 10 min. The resulting mixture was subjected to filtering for 30 min and the resulting products were dried in fluidized dryer. The dried products thus obtained (water content: 2.50%) were distributed for 10 min by using a vibrating distributor with a sieve having a pore size of 100 mesh without grinding. After the distribution, 995 g of the product (water content: 2.48%) under 100 mesh was 20 obtained. The results are shown in Table 1.

Examples 2 to 7 and Comparative Example

The reaction was carried out according to the same method described in Example 1 except that reaction temperature, the kind of a diluent gas and the 25 amount used thereof were changed. The results are shown in Table 1.

Table 1

	Diluent gas		Primary reaction		Secondary reaction		Tertiary reaction		Particle distribution of cellulose (under 100 mesh, %)
	Kind	Amount (kg)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	
Ex. 1	Dimethyl ether	1.5	40	60	60	100	80	180	99.5
Ex. 2	Dimethyl ether	1.0	40	60	60	100	80	180	99.5
Ex. 3	Dimethyl ether	0.5	40	60	60	180	80	180	99.6
Ex. 4	Dimethyl ether	0.1	40	30	70	120	90	60	99.5
Ex. 5	Dimethyl ether	1.0	45	60	60	180	90	60	99.4
Ex. 6	Dimethyl ether	1.5	45	60	60	180	90	60	99.5
Ex. 7	Dimethyl ether	0.0	40	60	60	120	90	60	99.6
Com Ex.	Dimethyl ether	3.0	60	60	80	60	90	180	45.5

As mentioned above, the method for the preparation of fine powdered

cellulose ethers of the present invention solves the problems of known methods that are economically unfavorable and complex. The method of the present invention can prepare the cellulose ether particles in the form of a hard fiber by regulating the amount of organic compounds in the synthetic process and efficiently controlling the 5 reaction temperature, which makes the process much simplified. Further, the method of the present invention is capable of determining the form of cellulose ether particles by regulating the amount used of a diluent gas, and is economically favorable to the point of expenses for running, maintenance and repair of equipment by introducing an epoch-making preparing process having no need of an additional 10 grinding step besides a simple drying step and reducing a running load on the equipment. Furthermore, the method of the present invention increases the productivity by reducing the time required for the process.

Since the fine powdered cellulose ether particles thus prepared have a larger surface area than the known cellulose ethers, they can be rapidly hydrated and 15 easily converted into a solution. Therefore, the cellulose ethers prepared according to the inventive method are suitable for preparing or coating a capsule in a medical industry as well as can be effectively used as a filler in a paste or a molding mixture together with mortar, gravel, cement or plaster and an additive in a synthetic resin.

20 While the embodiments of the subject invention have been described and illustrated, it is obvious that various changes and modifications can be made therein without departing from the spirit of the present invention which should be limited only by the scope of the appended claims.